

Fig. 1 Correlation between the yield of CH_3OH and the conduction bands of semiconductor catalysts. Dashed line denotes the standard redox potential of a $\text{CH}_3\text{OH}/\text{H}_2\text{CO}_3$ couple. Potentials are expressed against the normal hydrogen electrode (NHE).

illumination for 7 h, as shown in Table 1. Figure 1 shows the yields of methyl alcohol by photocatalytic reduction of carbon dioxide as a function of the energy levels of the conduction band of the semiconductor catalysts. The yields of methyl alcohol increase as the conduction band becomes more negative with respect to the redox potential of $\text{H}_2\text{CO}_3/\text{CH}_3\text{OH}$, whereas methyl alcohol was not produced in the presence of WO_3 catalyst which has a conduction band more positive than the redox potential of $\text{H}_2\text{CO}_3/\text{CH}_3\text{OH}$.

In experiments with semiconductor electrodes, carbon dioxide was reduced electrolytically to formic acid, formaldehyde, methyl alcohol and methane at the unilluminated TiO_2 electrode or at the illuminated p-type GaP electrode when both semiconductor electrodes were polarised at a potential of -1.5 V against a saturated calomel electrode for 2 h (Table 1). Thus electrons in the conduction band of semiconductor electrodes are able to reduce carbon dioxide in an aqueous solution.

It has been suggested that at semiconductor electrodes, the charge transfer rates between photogenerated carriers in semiconductors and the solution species depend on the correlation of energy levels between the semiconductor and the redox agents

in the solution¹¹⁻¹³. That is, the solution species of redox potential the more positive with respect to the conduction band level is better reduced at semiconductors. This hypothesis is illustrated in Fig. 2 which shows the energy correlation at the semiconductor-solution junction. When estimating charge transfer it is assumed that for semiconductor catalysts, as for semiconductor electrodes, photo-excited electrons in the more negative conduction band have the greater ability to reduce carbon dioxide in the solution.

Thus the photocatalytic reaction on a semiconductor catalyst appears to take place through the action of the photogenerated carriers (electrons and holes) acting as components of a local cell—reduction by electrons occurring in a conduction band and oxidation by holes in a valence band. The estimated quantum yields of production for photocatalytic reduction of carbon dioxide were $\sim 5.0 \times 10^{-4}$ for HCHO and 1.9×10^{-4} for CH_3OH with a TiO_2 catalyst, and 5.0×10^{-4} for HCHO and 4.5×10^{-3} for CH_3OH with SiC as catalyst, measured against the absorbable incident photons. We are now investigating the detailed dynamics of the photocatalytic reaction on the semiconductor catalysts.

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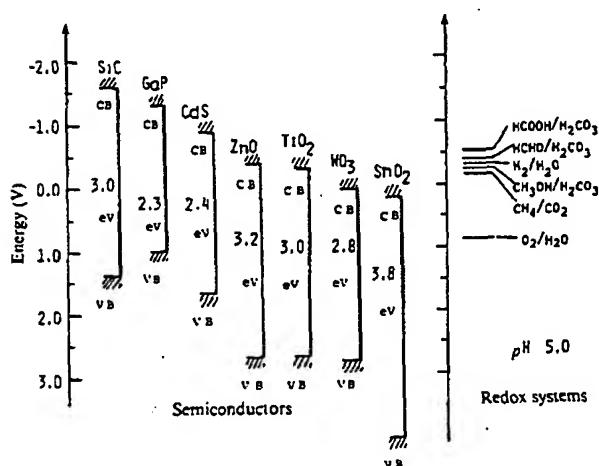


Fig. 2 A schematic illustration of the energy correlation between semiconductor catalysts and redox couples in water. CB and VB denote a conduction band and a valence band, respectively.

The design of solar conversion systems based on the photosynthetic primary reactions has attracted much attention recently. For instance, photoelectrolysis at a chlorophyll (Chl) α -water aggregate coated platinum electrode as a photocathode has been studied by Fong *et al.*¹⁻³, and simulation of the photoinduced electron transfer across the thylakoid membrane as well as of the biological ordered structure in a chloroplast has been attempted by Tien *et al.*^{4,5} using a Chl α -containing bilayer lipid membrane (BLM). We have already attempted to combine these different approaches⁶ by using a Chl α monolayer coated SnO_2 transparent electrode as a photoanode, and a maximum photocurrent quantum efficiency of 12–16% was attained with Chl α -stearic acid mixed monolayer systems. In that case, however, a decrease of the quantum efficiency was observed at Chl α -stearic acid molar ratios < 1.0 ; this might be due to the formation of pheophytin α and/or to a possible heterogeneity of the mixed monolayers. We describe here how we have overcome such problems by using a phospholipid instead of the fatty acid as a

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diluent for a Chl α monolayer. The hydrophobic interactions between Chl α and phospholipids have been well investigated both *in vivo* and *in vitro*, and the physical stability and photochemical activity of Chl α -synthetic lipid mixed layers were also confirmed in the BLM study⁷.

Chl α was prepared from spinach as previously reported⁶. Synthetic L- α -dipalmitoyl lecithin (DPL, Sigma) was used as a phospholipid without further purification. An SnO_2 optically transparent electrode (OTE)⁶ was used as a substrate of the monolayer deposition. The mixed monolayers of Chl α and DPL were prepared by spreading 2×10^{-4} M benzene solutions of Chl α and DPL in various molar ratios onto 10^{-3} M phosphate buffer solution (pH 7.5–8.0) in a Langmuir trough. A single layer of the mixed monolayer formed on the aqueous surface was deposited onto the SnO_2 OTE under the constant surface pressure of 20 dyn cm^{-1} . The electrochemical measurement setup was as reported previously⁶. The electrolyte solution used consisted of 0.1 M Na_2SO_4 , 0.025 M phosphate buffer (pH 6.9), and 0.05 M hydroquinone as a reducing agent, and was flushed with nitrogen throughout the experiments. Monochromatic light from a 500-W Xe-arc lamp irradiated the monolayer coated SnO_2 OTE and the photocurrent was measured by a Keithley picoammeter (Model 417) in a potentiostatic condition of +0.1 V versus saturated calomel electrode (SCE).

The surface pressure-area ($F-A$) characteristic of Chl α -DPL mixed monolayer is compared in Fig. 1 with that of pure Chl α ⁶. The stability of the mixed monolayer, even at pressures higher than 24 dyn cm^{-1} (the collapse pressure of Chl α monolayer), implies that the present Chl α -DPL mixed monolayer could form a homogeneous two-dimensional solution. This homogeneity can be also supported by the observed change in the absorption property of the mixed monolayer following the dilution of Chl α content. On decreasing the molar ratio of Chl α -DPL from 1:0 to 1:99, the peak position of the red absorption band was found to shift gradually from 675 nm due to an aggregated state of Chl α towards 665 nm due to the monomeric state, accompanying the decrease in absorbance in proportion to the surface concentration of Chl α . These physical and spectral properties indicate the formation of homogeneously mixed monolayer as reported for other Chl α -diluent systems^{8,9}.

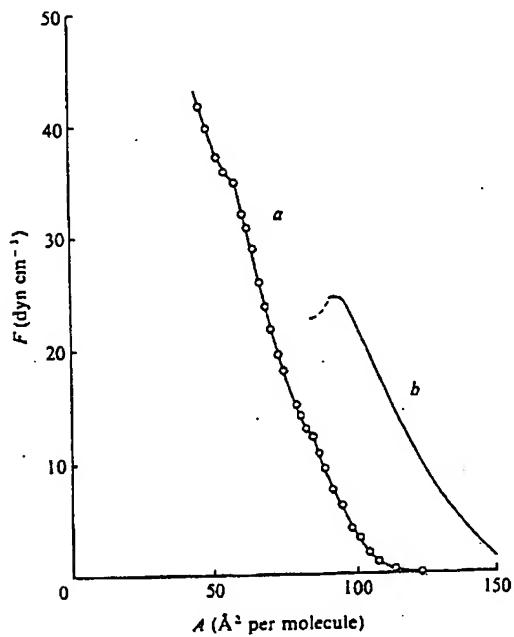


Fig. 1 $F-A$ characteristics of a Chl α -DPL (1:1) mixed monolayer and a Chl α monolayer: *a*, Chl α -DPL (1:1) mixed monolayer; *b*, pure Chl α monolayer. Aqueous phase, 10^{-3} M phosphate buffer (pH 7.5); air atmosphere at $25^\circ C$.

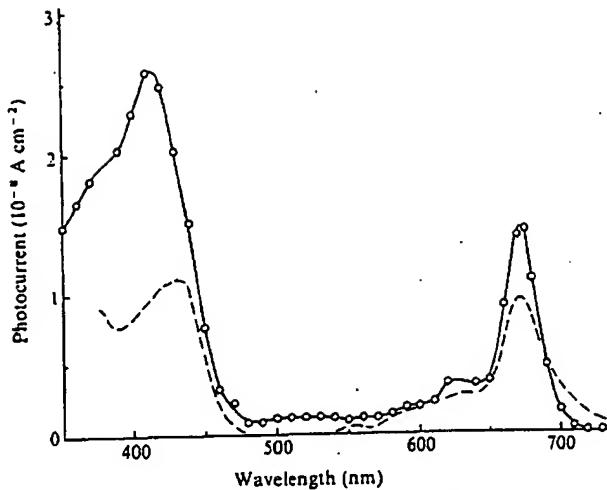


Fig. 2 Photocurrent spectrum at SnO_2 OTE deposited with mixed monolayer of Chl α -DPL (1:9). Dashed curve indicates the absorption spectrum of the mixed monolayer at the OTE-electrolyte interface. Composition of the electrolyte solution, 0.05 M hydroquinone, 0.1 M Na_2SO_4 , and 0.025 M phosphate buffer (pH 6.9); electrode potential 0.1 V versus SCE; incident flux of monochromatic light, 2×10^{14} photons $s^{-1} \text{cm}^{-2}$.

When a Chl α -DPL mixed monolayer was irradiated in the electrochemical cell, an anodic photocurrent was always obtained in accordance with the electron injection from excited Chl α into the conduction band of SnO_2 . A typical photocurrent spectrum, corrected for the slight background photocurrent of SnO_2 , for the mixed monolayer of molar ratio Chl α -DPL of 1:9 is shown in Fig. 2. The magnitude of photocurrent corresponds to a constant incident flux of 2×10^{14} photons $s^{-1} \text{cm}^{-2}$ at each wavelength. The photocurrent spectra coincided well with the absorption spectra of mixed monolayers at OTE-electrolyte interface. The quantum efficiencies of photocurrents were determined in terms of electrons flowing per absorbed photon, the latter could be estimated from the incident photon flux measured by chemical actinometry and from the monolayer absorbance at an OTE-electrolyte interface. The photocurrent quantum efficiencies obtained with mixed monolayers at different molar ratios are listed in Table 1, together with the calculated mean intermolecular distances between Chl α molecules. As the Chl α -Chl α intermolecular distance increases, the photocurrent efficiency also tends to increase, with a hypso- and bathochromic shift of the photocurrent peak positions in the red and blue regions, respectively. Such an enhancement of the quantum efficiency is attributable to the suppression of intermolecular energy transfer between Chl α molecules by the increase in its intermolecular distance, because the energy transfer inevitably accompanies an energy loss which eventually decrease the overall efficiency of electron injection from excited Chl α to SnO_2 . The concomitant shifts of photocurrent peak positions are compatible with the shifts in absorption peaks described above, and the absence of the characteristic peaks due to pheophytin α around 400–410 nm and 500–540 nm (ref. 10) in both photocurrent and absorption spectra of mixed monolayers indicates that the pheophytin formation is effectively suppressed in the present systems; a similar stability against the pheophytinisation was recently investigated by Iriyama (ref. 11 and personal communication).

The maximum efficiency of $25 \pm 5\%$ obtained in this work at neutral pH is relatively large, and almost twice that attained with the Chl α -stearic acid system⁶. Moreover, an examination of the pH dependence of the photocurrent showed that the quantum efficiency could reach $30 \pm 5\%$ when the experiment was done in the electrolyte solution at $pH \sim 5$. These values are sufficiently larger than the quantum conversion efficiencies reported ($10^{-3} \sim 10^{-1}$) (refs 3, 4, 12–14) with other solar conversion cells using Chl α as a photoreceptor.

Meilanov *et al.*¹⁵ in their attempt to verify the semiconductor model of photosynthesis, found a relatively high quantum efficiency (12–20%) for bulk photoconductive effects in metal-sandwiched dry Chl layers (0.3–2 μm thick) across which a high voltage (30–250 V) was applied. Our system is essentially different in that the photocurrent is produced by a direct electronic coupling between an excited Chl and the conduction band of SnO₂, not by an accelerating effect of the electric field across the Chl layer.

An extension of the present experiments to the construction of biomimetic membranes on SnO₂ OTE by incorporating other photosynthetically important compounds into the Chl *a*-DPL mixed monolayer would be highly promising in view of the *in vitro* simulation of the photosystem II in plant photosynthesis.

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Enhanced CO₂ greenhouse to compensate for reduced solar luminosity on early Earth

CURRENT models for the evolution of the Sun require an increase in solar luminosity by 25% since the formation of the Solar System¹. Such an increase in the solar constant should have profound effects on the terrestrial climate, but there is no evidence from the fossil record of a corresponding change in the Earth's global mean temperature². This apparent conflict cannot be explained by the apparent inability of solar models to account for the low observed neutrino flux³. Even models that are forced to fit the neutrino data require a similar increase in the solar luminosity. As Newman and Rood¹ state: "a faint young Sun is one of the most unavoidable consequences of stellar structure considerations". We discuss here whether CO₂-H₂O in a weakly reducing atmosphere could have caused this change in the early Earth's temperature by the so-called greenhouse effect.

Sagan and Mullen⁴ suggested that the solution must lie in a more efficient atmospheric greenhouse effect on Earth during the period when the solar luminosity was low. To increase the greenhouse effect, it is necessary to change the atmospheric composition, or density, or both. Sagan and Mullen⁴ postulated that the atmosphere was reducing during the early history of the Earth and found that a small amount of ammonia in the atmos-

sphere (mixing ratio 10⁻⁵–10⁻⁶) would provide the necessary opacity to outgoing infrared (IR) radiation to increase the mean surface temperature. In this model, the transition from reducing to oxidising conditions with the replacement of the NH₃-H₂O greenhouse by a CO₂-H₂O greenhouse comes about as a result of the development of widespread green plant photosynthesis 1,000–2,000 Myr ago. A similar route was invoked by Hart⁵, who developed a more detailed model for the evolution of the atmosphere.

We agree that an enhanced greenhouse effect caused by a change in atmospheric composition is a good solution to the solar constant dilemma, but we think the NH₃-H₂O model is unrealistic. Current thinking about the early atmosphere of the Earth is shifting away from the traditional view that called for a highly reduced mixture of methane, ammonia and hydrogen, for reasons summarised by Walker⁶. More recent data have simply added strength to Walker's conclusions. As the noble gases on Mars show the same pattern of relative abundances as they do on Earth and in the 'planetary component' of the meteoritic gases, whatever fractionation process caused this pattern must have occurred before planet formation⁷. This being the case, the cosmic abundance ratio of 1.6 × 10⁴ for H/Ne⁸ gives the maximum amount of hydrogen available for a 'captured' primitive atmosphere. Using the present atmospheric partial pressure of Ne (12.7 × 10⁻⁶ bar), the maximum hydrogen partial pressure on the primitive Earth from this source was 10 mbar. As Walker⁶ has pointed out, such an atmosphere would have dissipated in <10⁴ yr. The partial pressure of ammonia in this atmosphere would have been comparable to that of neon, but its lifetime against photodissociation would have been short and it would have been out of equilibrium with crustal rocks.

Photochemical calculations by Kuhn and Atreya⁹ indicate that ammonia would be irreversibly converted to N₂ on the primitive Earth in <40 yr if the mixing ratio were ≤ 10⁻⁴. Eugster¹⁰ has investigated the stability of ammonia on the primitive Earth and concluded that a mixture of N₂ and H₂ will predominate over ammonia in a normal crustal environment. Outgassing of ammonia after the last phase of accretion (or after differentiation, choosing either an inhomogeneous or homogeneous model for planet formation) seems precluded by the lack of free iron in the upper mantle¹¹. As life must have begun after this phase in the planet's history, it seems reasonable to agree with Eugster¹⁰ that any initial ammonia in the atmosphere "was oxidised to nitrogen long before the origin of life". Small amounts of methane and ammonia may have been transiently present in later times as a result of meteoritic and cometary impact, but lunar evidence indicates that bombardment rates must have been close to their present low values ~3,600 Myr ago¹¹.

In fact, the idea that the chemistry preceding the origin of life must have occurred in highly reducing conditions supported the traditional view of the composition of the early atmosphere¹². But there have been sufficient demonstrations that pathways towards the formation of essential pre-life compounds can occur only in weakly reducing conditions for this argument to have lost its original force. For example, Abelson¹³ was able to produce amino acids from the UV irradiation of a mixture of CO₂, CO, N₂, H₂O and just 1–10% H₂. This seems a much more reasonable composition for the post-accretion (or post-differentiation) atmosphere of the primitive Earth^{6,10}. It is especially unlikely that the ammonia-containing mixture invoked by Sagan and Mullen⁴ (or ammonia plus methane suggested by Hart⁵) would last for 2,000–3,000 Myr after formation of the planet. But can this weakly reducing atmosphere provide the required greenhouse effect? The answer depends on carbon dioxide and water vapour, as the other gases are ineffective absorbers of IR radiation.

We have tested this possibility by assuming that the concentration of CO₂ in the early atmosphere was much higher than the present value. We have coupled the evolutionary model for the CO₂ abundance used by Hart⁵ with a radiative-convective CO₂-climate model. (We used the model as in Augustsson and

